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Development of partial oxy-combustion technology: New solvents applied to CO_2 capture in fossil-fuels power plants

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Abstract

Carbon Capture and Storage Technologies (CCS) applied to fossil-fuels power plants have shown some issues that has not been solved yet. Post-combustion using amine-based chemical absorption is a mature and industrially developed technology but the solvent regeneration requires a high-intensive energy consumption. On the other hand, oxy-combustion requires a large amount of high-purity oxygen that can only be supplied by cryogenics. Therefore, the oxygen production is its higher energy penalty. Partial oxy-combustion is a hybrid technology between both technologies that proposes an optimized operation that can lead to further reductions on the overall energy consumption. A comprehensive study of solvents applied in CO_2 capture have been carried out under higher CO_2 partial pressures. Two new solvents, namely HYBRID-1 and HYBRID-2 have been formulated and tested. Results extracted from the experiments with MEA have shown absorption improvements in higher CO_2 concentrated flue gas cases in comparison with air-fired cases (15% v/v CO_2). In particular, HYBRID-1 reported the most promising results in terms of equilibrium CO_2 loading and CO_2 absorption rate compared with MEA. HYBRID-1 have been considered as a potential solvent for partial oxy-combustion applications

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Keywords: Partial oxy-combustion; CCS; CO_2 capture; solvents

1. Introduction

Post-combustion and oxy-combustion have been considered as promising technologies to reduce CO_2 emissions from fossil-fuel power plants [1]. CO_2 capture using chemical absorption by aqueous amine-solutions is applicable for post-combustion capture applications even the exhaust gas conditions: low CO_2 partial pressure, large volume of flue gas and the presence of pollutants such as SO_2 and NO_X.

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The higher energy penalty is one of the most significant issues hindering a large deployment of this technology, particularly the energy consumption related to solvent regeneration. Monoethanoamine (MEA) aqueous solution (30% w/w in water) requires 4.2 GJ per t CO_2 captured [2-3]. Several configurations have been proposed to achieve optimal process integration, decreasing the reboiler duty up to 2.22 GJ/t CO_2 capture in some cases [3]. Higher temperature and pressure at the stripping column can lead to further reductions of the reboiler duty, being limited by the solvent degradation [4].

Oxy-combustion is based on the use of high purity O_2 as oxidizer instead of air. Flue gas recirculation (FGR) is employed to control temperature profiles along the boiler. A high CO_2 concentrated flue gas is provided and, therefore, separation process is not required. In oxy-combustion case, O_2 separation from air produces the highest energy penalty from the global process. Efforts have focused on both thermal integration to reduce energy consumption of cryogenic air separation [5] and development of new technologies to produce the large amounts of O_2 required such as ion transport membranes (ITM), vacuum pressure swing adsorption (VPSA) and temperature swing adsorption (TSA) [6-9].

Partial O_2-fired coal power plant with post-combustion CO_2 capture, namely partial oxy-combustion in this work, is proposed as a new alternative from traditional CCS technologies described above [6]. It consists of a hybrid technology between post-combustion and oxy-combustion which is based on the use of oxygen-enriched air during the combustion process followed by a CO_2 capture process by chemical absorption. It is expected that this alternative minimizes investment and operating costs and increases energy efficiency of CO_2 capture in fossil-fuels power plants [10]. Reboiler duty can be reduced up to 30% in partial oxy-combustion operations in comparison with post-combustion capture based on chemical absorption using MEA [6].Several authors have shown that partial oxy-combustion is a technically and economically feasible technology that can provide significantly reductions of both electricity price and CO_2 capture cost [6,11]. Partial oxy-combustion offers some potential advantages for CCS technologies. In particular, novel O_2 separation technologies such as adsorption and membrane separation can be proposed to produce the oxygen-enriched air required for the combustion process whereas higher CO_2 partial pressure in the flue gas leads to further improvements in the CO_2 chemical absorption process. This paper aims to contribute to the evaluation of the feasibility of partial oxy-combustion technology applied for existing power plants. New solvents and amine-based blends have been tested under higher CO_2 concentration in the flue gas. Novel absorber configurations and higher temperature and pressure stripping conditions have been settled up to minimize the energy consumption related to solvent regeneration (GJ/ t CO_2 captured).

2. Experimental setup

In this work, more than 20 solvents and blends have been selected from the literature. Monoethanolamine (MEA), N-Methyldiethanolamine (MDEA), Triethanolamine (TEA) and novel solvents referenced in recent works such as Piperazine (PZ) and 2-amino-2-methyl-1 propanol (AMP) have been tested. All the reagents were supplied by Acros Organics with a minimum purity of 99% without further purification. Solvents and blends were prepared in aqueous solution using deionized water.

Firstly, physical properties and equilibrium curves determinations were carried out for each solvent and blend tested. Density were determined using a picnometer and a Höppler apparatus was used for viscosity determinations. PH was also studied. Experiments were carried out at both ambient temperature and absorption temperature, typically 50ºC. Maximum solubility in water of solid solvents, such as potassium carbonate and PZ, was determined following the method proposed by Bisnhoi et al. [12]. CO_2 solubility was evaluated using VLE apparatus described by Derks et al. [13] VLE curves were previously compared with MEA to choose solvents which showed better behavior than MEA under partial oxy-combustion conditions.

The selected solvents were tested in a lab-scale apparatus operating under semi-batch conditions (Fig. 1). The semi-batch apparatus consists of a stirred 250-mL vessel immersed in a bath heater to adjust the desired temperature. Synthetic flue gas varies from 15% vol to 60% vol CO_2 balanced with N_2, being saturated with water before. 2

L/min are bubbled into the vessel where solvents are placed. The gas leaving the vessel is monitoring with a FTIR analyzer to determine CO_2 concentration in the exhaust gas. A pressure transducer is used to record pressure data during the experiments. Gas phase was evaluated by CO_2 absorption rate determinations from FTIR measurements. Liquid samples were withdrawn during the experiments to determine the CO_2 loading (mole CO_2 per mole absorbent) using a TOC analyzer in order to evaluate liquid phase behavior.

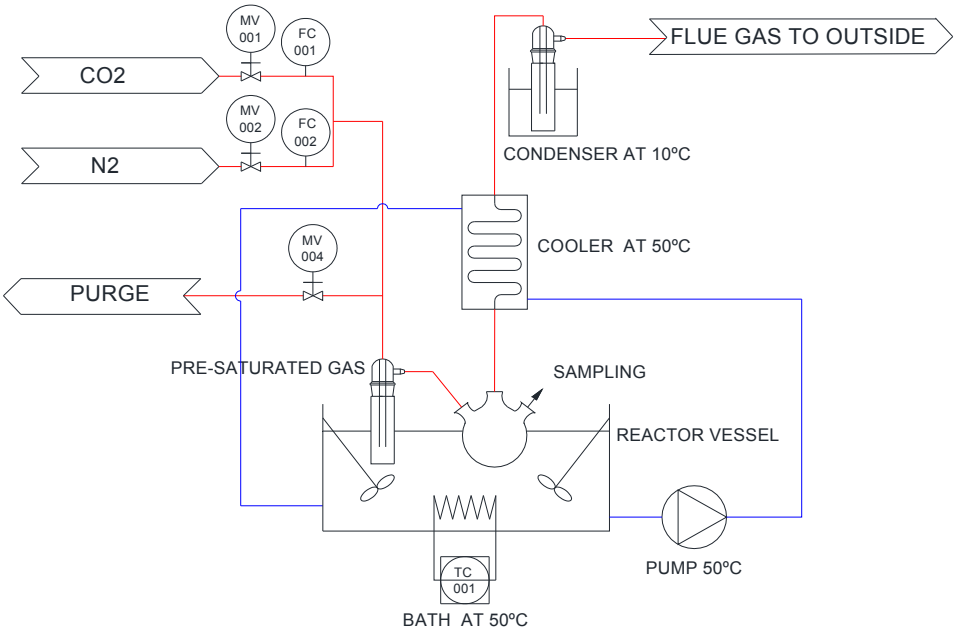

Fig. 1. Semi-batch apparatus sketch.

3. Results

3.1. MEA test campaign

MEA is considered as benchmark for acid gas cleaning based on chemical absorption. In this paper, MEA was tested to elaborate a preliminary evaluation of solvents operated under partial oxy-combustion conditions. As mentioned above, four levels of CO_2-enriched flue gas were set up during the experiments where CO_2 concentration varied from 15% to 60% v/v. Fig. 2 shows the CO_2 absorption rate, measured as ml CO_2(g)/min, during the experiments.

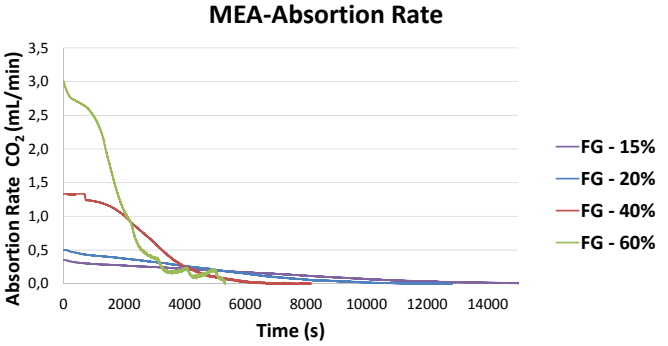

Fig. 2. Evolution of CO_2 absorption rate during MEA experiments in the semi-batch apparatus.

As can be seen, higher CO_2 partial pressure in the flue gas provided higher absorption rates. In particular, FG - 20% case enhanced slightly the CO_2 absorption rate in comparison with FG – 15% that lead faster to an equilibrium stage. This phenomena is increased in FG – 40% and FG – 60% cases where a modified behavior of the absorption process is observed.

Fig. 3 represents the evolution of the CO_2 loading for each case. CO_2 loading and its slope were improved significantly in higher CO_2 partial pressures cases. CO_2 loading at equilibrium was shifted to higher values, from 0.47 to 0.6 in FG – 15% and FG – 60%, respectively and the CO_2 absorption rate, measured from the liquid phase, was five times higher from FG – 15% to FG – 60%. The use of higher CO_2 partial pressure produces an absorption process enhancement that is more significant from FG – 20% case: equilibrium loading increased from 0.52 to 0.6 and the slope improved up to 45% in FG - 60% case.

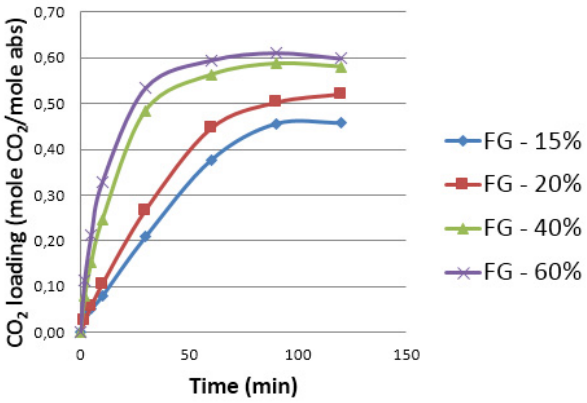

Fig. 3. CO_2 loading evolution during MEA experiments in the semi-batch apparatus.

3.2. New solvents applied in partial oxy-combustion

New solvents, namely HYBRID-1 and HYBRID-2, have been proposed to be applied in CO_2 capture process under partial oxy-combustion conditions. Selection criteria were based on obtaining blends that showed physical properties similar to those regarding MEA: high stability, solubility in water, non-excessive viscosity and ph below 12.5 in order to limit corrosion issues. High cyclic capacity have been also considered as a key criterion. The aim is to formulate a new solvent that improves the benefits MEA showed under higher CO_2 concentrated flue gas in terms of maximum CO_2 loading (equilibrium), cyclic capacity and CO_2 absorption rate.

Both new solvents were tested at the same operating conditions than MEA cases. Fig. 4 summarized the results obtained after the test campaign were carried out. In terms of CO_2 loading, HYBRID-1 reported values from 0.66 to 0.8, showing a gap of 0.2 points over MEA tests in all the cases, whereas HYBRID-2 provided the same CO_2 loading than MEA tests except for FG – 15% case where a 0.5 mole CO_2 per mole solvent was obtained.

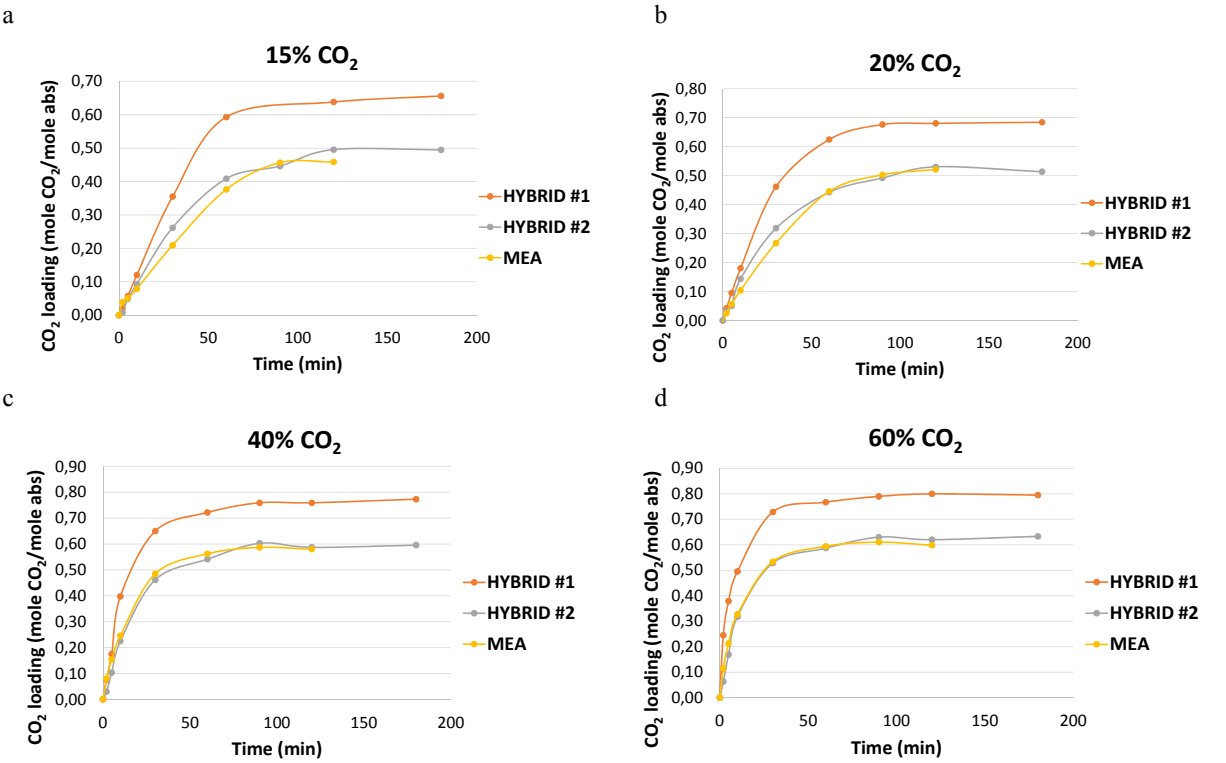

Fig. 4. CO_2 loading change during HYBRID-1 and HYBRID-2 experiments in the semi-batch apparatus for different CO_2 concentration in the flue gas: (a) 15%; (b) 20%; (c) 40%; (d) 60%.

As MEA test campaign pointed out before, both solvents improved their absorption behavior at higher CO_2 partial pressure. HYBRID-1 resulted in a higher slope tan MEA (Fig. 4), being increased up to two times in all the cases. Therefore, HYBRID-1 is considered as a potential solvent for partial oxy-combustion applications. It showed the best behavior among all the solvents tested. Besides, HYBRID-2 showed no differences in kinetic and absorption behavior than MEA and it was not recommended as solvent for partial oxy-combustion.

4. Conclusions

Partial oxy-combustion is considered as a potential option for CO_2 capture applied in fossil-fuels power plants. The aim of this technology is reduced significantly CO_2 capture cost based on an optimization of both process, O_2-enriched air production and CO_2 separation. Experimental tests carried out with MEA have shown promising results, producing an enhancement of the CO_2 absorption process. Absorption rates can be increased up to five times from 15% to 60% CO_2 concentration in the flue gas. Among all the solvent tested, two new blends have been proposed, HYBRID-1 and HYBRID-2. HYBRID-2 obtained no improvements in comparison with MEA cases. On the other hand, HYBRID-1 resulted in a higher CO_2 loading at equilibrium and CO_2 absorption rate two times faster than MEA. HYBRID-1 have been considered as a potential solvent for partial oxy-combustion applications. Further investigations at pilot plant scale will be set up to confirm that promising results.

Acknowledgements

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